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Preparation of TiO_2-enriched $CaCu_3Mn_{0.1}Ti_{3.9}O_{12}$ ceramics and their dielectric properties

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Abstract

TiO_2-enriched $CaCu_3(Mn_{0.1}Ti_{3.9})O_{12}$ (CCMTO) ceramics have been prepared by a two-step method. X-ray diffraction (XRD) and TEM results indicate that TiO_2 particles were partially coated on the surface of CCMTO powders. The dielectric spectra of TiO_2-enriched CCMTO samples showed that the dielectric constant was almost independent of the measured frequency and the dielectric loss was markedly suppressed by increasing the addition of TiO_2. The grain activation energy was calculated and an increase in energy was observed with the addition of TiO_2. This transformation gave influence to grain charge mobility and resulted in transformed dielectric behaviors.

Keywords: CCTO; TiO_2; Dielectric; Activation energy

1. Introduction

Recently, miniaturization of electronic devices, such as capacitors and memory storage tools, is strongly required for their progress. To achieve this goal, high dielectric constant materials with good temperature and frequency stability are strongly desired. It is well known that $ATiO_3$ based-perovskite oxides (where A = Ba, Sr, Pb) exhibit high dielectric constants. However, the attractive dielectric properties are always associated with ferroelectric or relaxor properties and remain as a function of temperature caused by the ferroelectric transition. In 2000, Subramanian discovered that oxide-based-perovskite-like (with general formula $AA'_3B_4O_{12}$) $CaCuTi_4O_{12}$ ceramics (CCTO) exhibited a gigantic dielectric permittivity of over 10^4, which are almost constant in the temperature range from 100 to 400 K and do not show ferroelectric transition behavior.[1,2] These interesting dielectric properties of CCTO have attracted lots of studies and discussions about the origin of its unusual dielectric properties.[3,4] A unit cell of CCTO ceramics contains tilted TiO_6 octahedral with square planer Cu atoms on A′-site. At first, intrinsic polarization, which generates from displacement of off-centered Ti ions, was considered the origin of the dielectric properties. However, extrinsic polarization induced from internal barrier layer structure is regarded as the origin of dielectric properties now. Some experimental results indicated that the existence of semi-conductive grain and insulative grain boundaries in bulk CCTO ceramics resulted in Internal Barrier Layer Capacitance (IBLC) effect. This IBLC effect is strongly related to CCTO's dielectric behavior.[3,5,6] Two plausible models were also established to explain CCTO semi-conducting grains, one based on oxygen loss, and the other based on cation nonstoichiometry.[6] Formation of CCTO semi-conducting grains are explained by a Cu oxidation process. During the heating process, Cu^{2+} becomes unstable and reduced to Cu^{1+}. This causes the Ti^{4+} ion to substitute for Cu^{2+} in order to maintain the oxidation state of the Cu site. Therefore, the ionic formula of CCTO can be expressed as $Ca^{2+}(Cu_{1-3x}{}^{2+}Cu_{2x}{}^{1+}Ti_x{}^{4+})_3Ti_4{}^{4+}O_{12}$ at high temperatures. Conversely, during the cooling process, Cu^{1+} is oxidized to Cu^{2+}. At this time, electrons move into the Ti 3d band and finally form $Ca^{2+}(Cu_{1-x}{}^{2+}Ti_x{}^{4+})_3(Ti_{6x}{}^{3+}Ti_{4-6x}{}^{4+})O_{12}$ at low temperatures. Ti^{3+} therefore represents the charge carrier and exhibits semi-conductive grains.[7,8] Consequently, the

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CCTO grain boundaries behave as n–i–n interface traps associated with a Schottky barrier, in which the grains have n-type conduction.[5,9]

Based on these findings, numerous previous reports were also concentrated on the dielectric behavior of the doped CCTO ceramics.[10–12] Mn- and Fe-doped CCTO cause great interest due to their suppressed dielectric constants.[11,12] On the other hand, Lin et al. showed that internal potential barrier height in grain boundaries can be increased by TiO_2-doping and decreased by Mn-doping.[13,14] These results indicated that internal potential barrier structures can be tuned by the doping process. Therefore, investigation on doped CCTO ceramics is expected as an efficient way to understand the relationship between dielectric behavior and the potential barrier structure of CCTO.

In this study, Mn-doped CCTO (CCMTO) powder was synthesized and then TiO_2-enriched CCMTO (TCCMTO) ceramics were fabricated by a chemical synthesis combined with a traditional ceramics processing.

2. Experimental procedure

$CaCO_3$, CuO, TiO_2 and MnO_2 were used as raw materials. $CaCu_3Mn_{0.1}Ti_{3.9}O_{12}$ was fabricated by a conventional solid-state sintering method. The obtained CCMTO powder was crushed by ball-milling again for 24 h. The dried CCMTO powder was then dispersed in $[CH_3[CH_2]_3O]_4Ti$-ethylene glycol solution (pH ∼ 4). Next, we slowly added NH_4HCO_3 in the above solution. The Ti^{4+} was precipitated as $Ti(OH)_4$ around the surface of CCMTO particles, and remained as mixed precipitates at 95 °C for 5 h. The dried powder was fired at 700 °C for 5 h to form TiO_2-coated CCMTO powders. Finally, TiO_2-CCMTO ceramics can be obtained after sintering at 1100 °C for 10 h.

To evaluate the phase composition of the synthesized powder, XRD patterns were obtained by Rigaku D/MAX-2500 at 40 kV and 100 mA (Cu Kα radiation). TEM images were performed to investigate the microstructure of synthesized powder by JEOL-2011. SEM-EDS were employed to investigate microstructure and composition of bulk ceramics. The dielectric properties of bulk specimens were investigated by HP 4194A gain phase analyzer over a frequency range from 10^3 to 10^7 Hz and at an oscillation voltage of 1.0 V. To understand the origin of dielectric properties, impedance spectrum at various temperatures were performed in the frequency range from 10^2 to 10^7 Hz by HP 4192A.

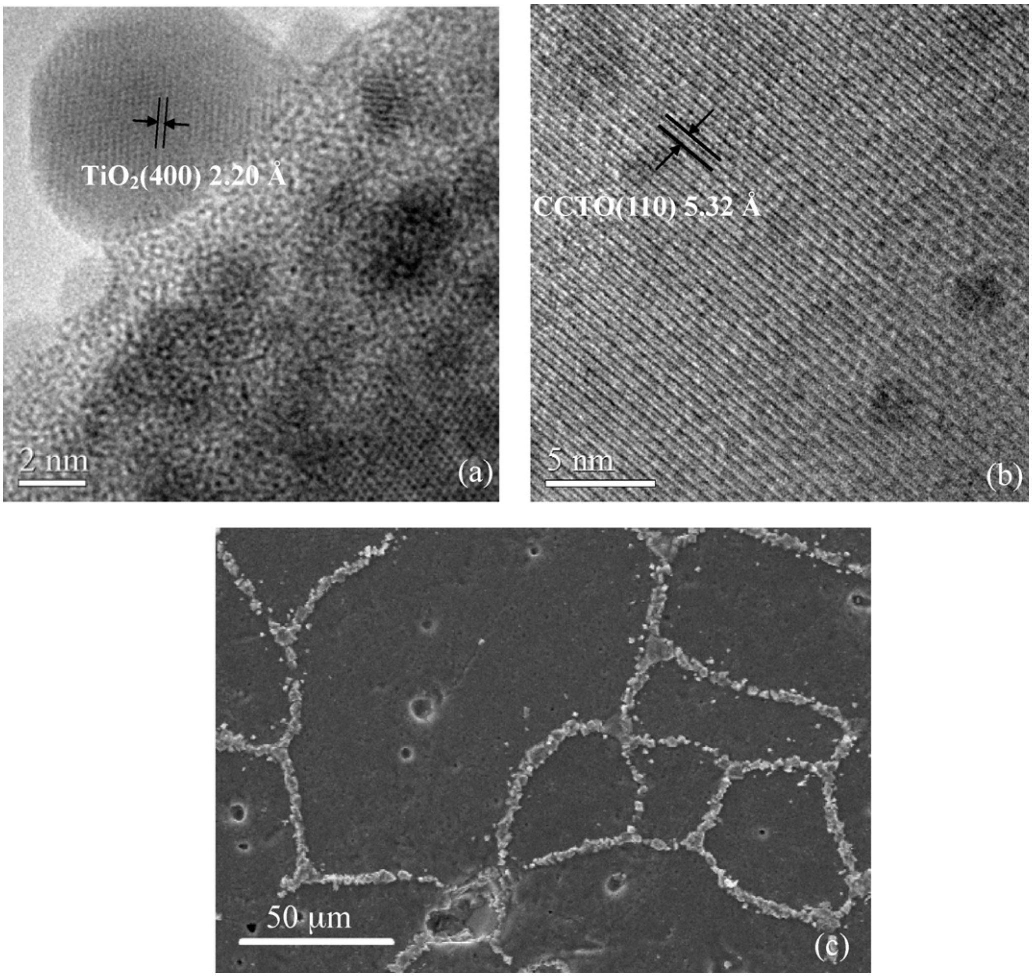

Fig. 1. HRTEM images of synthesized TCCMTO-3 precursor powders and SEM images of the surface of sintered bulk; (a) TiO_2 small particles coated on the CCMTO grain, (b) crystal lattice of CCMTO grain and (c) the surface of TCCMTO-3 bulk.

3. Result and discussion

Four kinds of TiO_2-enriched CCMTO ceramics samples with the nominal composition of 0%TiO_2-CCMTO (TCCMTO-0), 3%TiO_2-CCMTO (TCCMTO-1), 15%TiO_2-CCMTO (TCCMTO-2), 27%TiO_2-CCMTO (TCCMTO-3) have been prepared.

Fig. 1 shows the HRTEM images of the surface morphology of the calcined TCCMTO-3 powder. As shown in Fig. 1(a), numerous small particles were precipitated around the surface of larger CCMTO grains. Fig. 1(b) shows that the lattice spacing of the inner big grain was confirmed to be 5.32 Å corresponding to the (1 1 0) face of CCTO. The lattice spacing of the small particle was 2.20 Å, and corresponds to the (4 0 0) face of TiO_2 anatase. These results illustrated that a lot of TiO_2 small particles precipitated around the larger CCMTO grains. Fig. 1(c) shows the SEM images of the sintered TCCMTO-3 specimen. As shown in the figure, dense bulk ceramics were fabricated successfully with the secondary phase within the grain boundaries. The microstructure of others sample was the same as TCCMTO-3. The grain boundary thicknesses of each specimens were 2.75 μm (TCCMTO-0), 2.61 μm (TCCMTO-1), 3.38 μm (TCCMTO-2), 5.21 μm (TCCMTO-3), respectively.

XRD patterns of the synthesized TCCMTO powders are shown in Fig. 2. As shown in the figure, the main phase of the specimens was the CCTO phase. The Cu_2TiO_3 secondary phase that was generated by Mn-doping was also observed. Additionally, by increasing the amount of TiO_2 a tiny peak of TiO_2 was more easily observed.

Fig. 3 shows the dielectric properties of bulk TCCMTO ceramics in the frequency range from 10^3 to 10^7 Hz at room temperature. The results shown in Fig. 3(a) indicated that the dielectric constant decreased with increasing frequency from the value of 110 in 10^3 Hz to 70 in 10^7 Hz. However, the TiO_2-enriched CCMTO samples are independent of frequency in this measured frequency range. Additionally, the dielectric loss shown in Fig. 3(b) also decreased from 0.120 of TCCMTO-0 to 0.022 of TCCMTO-3 at 10^4 Hz due to the increase of TiO_2.

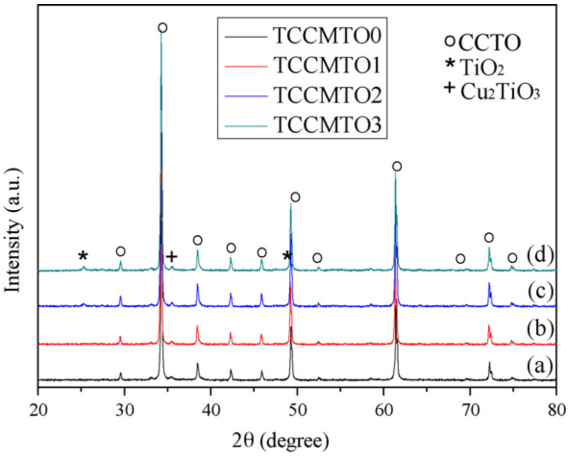

Fig. 2. XRD profiles of each specimen (a) TCCMTO-0, (b) TCCMTO-1, (c) TCCMTO-2, (d) TCCMTO-3.

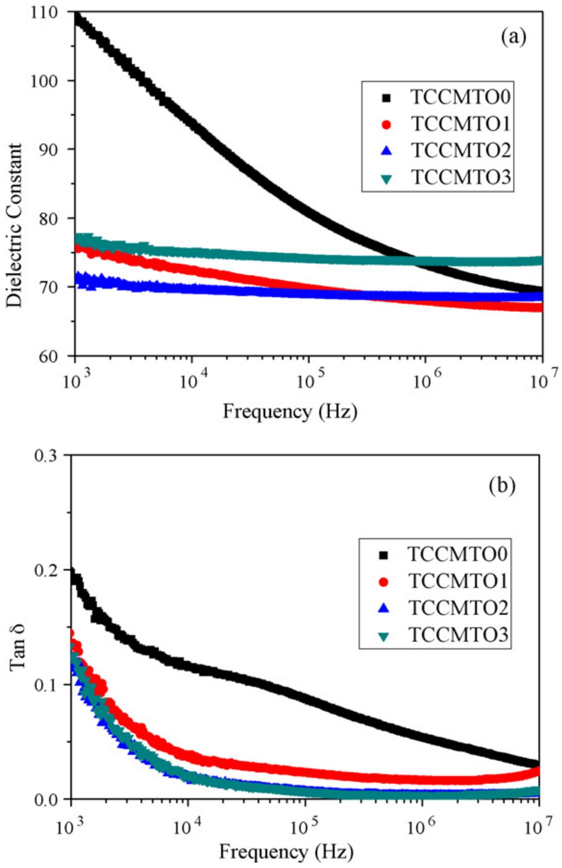

Fig. 3. The dielectric spectra of various ceramic specimens (a) dielectric constant and (b) dielectric loss.

Fig. 4 shows a combined (M'', Z'')–f spectroscopic plots of TCCMTO-3 specimens at 423 K. Two peaks were observed in the Z''–f plot. The M'' peak frequency, at around 30 kHz, was similar to that of the Z''–f plot, which corresponds with previous reports. [6] Two peaks in the Z''–f plot are defined as the grain response of the higher frequency peak and the boundary response of the lower frequency peak. Fig. 5 shows M''–f spectroscopic plots of specimens between 100 and 150 °C. The peak

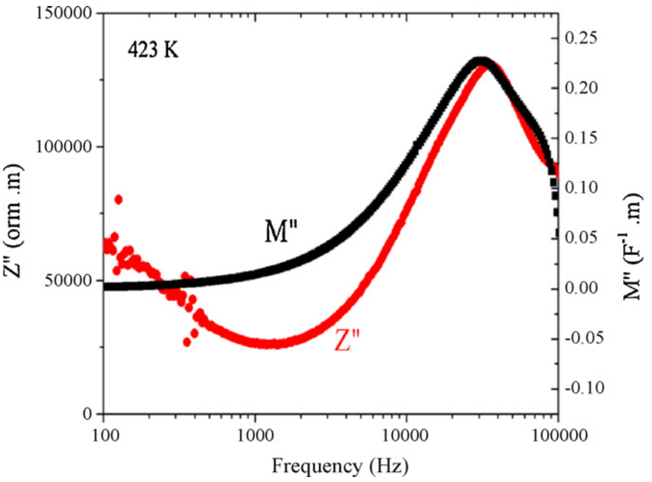

Fig. 4. A combined (M'', Z'')–f plots of TCCMTO-3 specimen at 423 K.

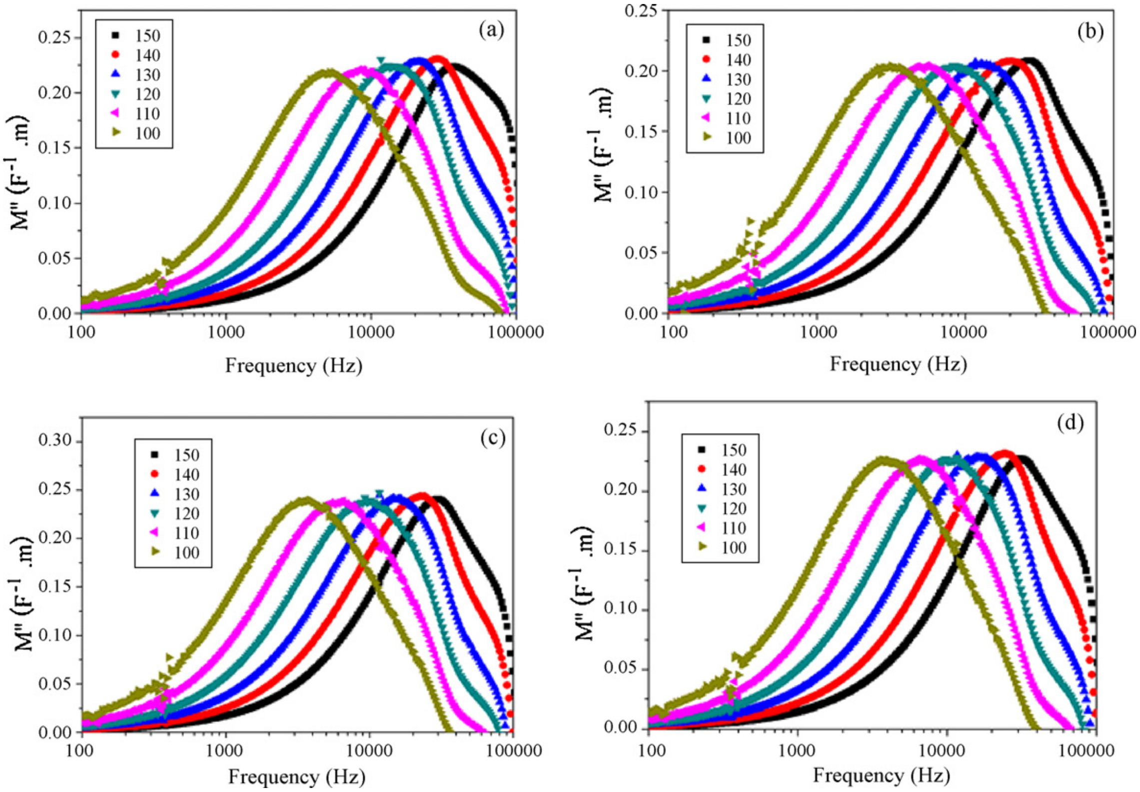

Fig. 5. M''–f plots of TCCMTO specimens. (a)TCCMTO-0, (b)TCCMTO-1, (c)TCCMTO-2, (d)TCCMTO-3.

frequencies were shifted to higher frequencies with increasing temperature.

Local activation energies were calculated to check internal barrier structure. Grain resistivity was calculated by using Eqs. (1) and (2).

$$C = \frac{1}{2M''_{\max}} \tag{1}$$

$$R = -\frac{1}{\omega_{\max} C} \tag{2}$$

Local activation energy can be calculated by using following equation.

$$\log \sigma \propto -\frac{E_a}{k_B T} \tag{3}$$

where k_B is Boltzmann coefficient, T is absolute temperature, and E_a is the activation energy. According to (3), the activation energy was determined by calculating the slope of $\log \sigma$ vs $1/T$. Fig. 6 shows $\log \sigma$ vs $1/T$ plots of the grain phase. The activation energy of the grain phase was increased with increasing TiO_2, from 0.229 eV of TCCMTO-0 to 0.254 eV of TCCMTO-3.

As mentioned before, the conductivity in the CCTO system is greatly related with trivalent titanium. During the fabrication process, Ti^{4+} appears with the reduction of Cu^{2+} to Cu^{1+} at high temperatures according to Eq. (4).

$$3Cu^{2+} \rightarrow 2Cu^{+} + Ti^{4+} \tag{4}$$

This Cu^{+} was oxidized during the cooling process with the reduction of Ti^{4+} to Ti^{3+} according to Eq. (5).

$$Cu^{+} + Ti^{4+} \rightarrow Cu^{2+} + Ti^{3+} \tag{5}$$

This trivalent titanium has electrons in the 3d Ti conduction band, which contributed to the bulk conductivity. Previous reports showed us that electrical properties in the CCTO systems can be easily transformed by a small amount of impurities.[12,14] In this study, as shown in boundary thickness, added TiO_2 tended to exist at grain boundary regions. Previous reports showed trace Ti substitution in grain boundaries was enough to transform

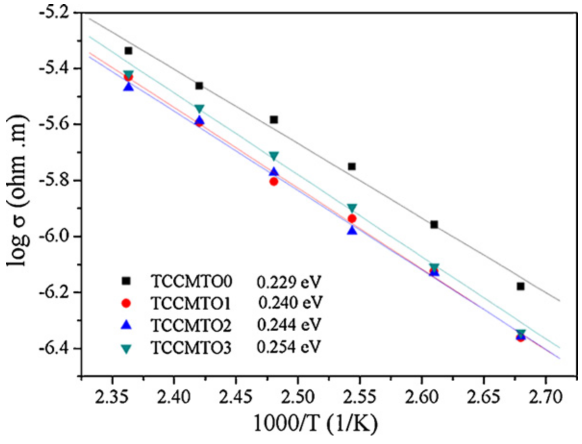

Fig. 6. The Arrhenius plots of grain TCCMTO specimens.

their conductivity. Therefore, added TiO_2 dispersed into the grain boundaries, transformed the conductivity of grain regions.

The suppressed dielectric constant and dielectric loss were explained by the change of grain activation energy. As shown in Fig. 6, grain activation energy was increased by TiO_2 addition. This transformation gave lots of influence to grain charge mobility. The driving force of the grain charge mobility was explained by the hopping conduction model due to peak frequency temperature dependence. Charge mobility is expressed by the following Eqs. (6) and (7).

$$\mu = \frac{ea^2 P}{kT} \tag{6}$$

$$P = \nu e^{-U/kT} \tag{7}$$

where μ is charge mobility, a is hopping distance, ν is frequency and U is activation energy. According to the above equations, charge mobility is decreased when activation energy is increased. Therefore, grain charge mobility was considered to be suppressed with increasing TiO_2 addition. The dielectric polarization of CCTO ceramics depends on the grain phase because dielectric polarization due to the IBLC effect occurs at the grain phase. As a result, suppressed grain charge mobility should lead to suppressed dielectric polarization, and result in a decreasing dielectric constant. In addition, this grain charge mobility transformation also gave influence to dielectric loss. Dielectric relaxation frequency is expressed as the reciprocal of dielectric relaxation time. The suppressed grain charge mobility made dielectric relaxation time increase, and resulted in lower dielectric relaxation frequencies. Therefore dielectric loss was suppressed in this study.

4. Conclusion

Fabricated TCCMTO ceramics exhibit excellent dielectric constants, which are independent of frequency and also experienced suppressed dielectric loss. Each TCCMTO ceramic had grain and boundary phases, and added TiO_2 tended to exist in the boundary phase. Trace Ti addition was found to be enough to transform grain conductivity. The addition of TiO_2 in the grain phase increased the grain activation energy, and decreased the grain charge mobility. This transformation gave influence to the formation of dielectric polarization and resulted in attractive dielectric properties which were observed in this research.

Acknowledgements

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